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Determination of four heterocyclic insecticides by ionic liquid dispersive liquid–liquid microextraction in water samples

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ABSTRACT

A novel microextraction method termed ionic liquid dispersive liquid–liquid microextraction (IL-DLLME) combining high-performance liquid chromatography with diode array detection (HPLC-DAD) was developed for the determination of insecticides in water samples. Four heterocyclic insecticides (fipronil, chlorfenapyr, buprofezin, and hexythiazox) were selected as the model compounds for validating this new method. This technique combines extraction and concentration of the analytes into one step, and the ionic liquid was used instead of a volatile organic solvent as the extraction solvent. Several important parameters influencing the IL-DLLME extraction efficiency such as the volume of extraction solvent, the type and volume of disperser solvent, extraction time, centrifugation time, salt effect as well as acid addition were investigated. Under the optimized conditions, good enrichment factors (209–276) and accepted recoveries (79–110%) were obtained for the extraction of the target analytes in water samples. The calibration curves were linear with correlation coefficient ranged from 0.9947 to 0.9973 in the concentration level of 2–100 μg/L, and the relative standard deviations (RSDs, $n = 5$) were 4.5–10.7%. The limits of detection for the four insecticides were 0.53–1.28 μg/L at a signal-to-noise ratio (S/N) of 3.

1. Introduction

Fipronil, chlorfenapyr, buprofezin, and hexythiazox are widely used heterocyclic insecticides to control pests of a variety of food crops and showed useful insecticidal utility. Although these compounds play important roles in agricultural practices, they exhibit toxic or other undesirable side-effect on non-target organism [1–3]. The extensive or inappropriate use of the insecticides leads to the insecticides and their metabolites' transfer to the environment, which contaminate the environment. Some of the toxicities of these insecticides were observed in mammals [4], aquatic organisms [5] and benefit insects such as beetles [6]. These insecticides' residues were found in vegetables, agricultural products and environmental soil or waters [7–9]. Therefore, increased monitoring efforts are required to illuminate the effects of these compounds and to evaluate the risk to human health. Sample preparation procedures before instrumental analysis are usually necessary. Liquid–liquid extraction (LLE) has been a typical sample preparation approaches and been used most widely [10,11]. Solid-phase extraction (SPE) developed as the alternative method has been applied in various environmental analytical applications [12–15]. However, both techniques require large volumes of toxic solvent which is unfriendly to the environment and the complicated procedures are normally tedious and time-consuming.

Impelled by the need to address these drawbacks, microextraction gradually evolves as a popular technique. Single-drop microextraction (SDME) as the miniaturized LLE accomplished by using a single-drop water insoluble solvent [16–18] has attracted great attention due to its merits of being simple, rapid, and only use small amounts of organic solvent. The main shortcoming of the SDME process is the instability of the drop and the sensitivity is low in high-performance liquid chromatography (HPLC) since the amount of the extraction is relatively small (1–2 μL).

DLLME is a novel microextraction method recently developed by Assadi and co-workers [19,20], and it has been applied for determination of polycyclic aromatic hydrocarbons (PAHs) [21], organophosphorus pesticides (OPPs) [22], chlorobenzenes [23], chlorophenols [24], phenols [25], and trihalomethanes [26], methomyl [27], phthalate esters [28], anilines [29], polybrominated diphenyl ethers [30] in liquid samples as well as in organic phosphorus watermelon and cucumber [31]. It was performed by injecting a mixture of extraction and dispersive solvent into aqueous samples, the cloudy solution quickly formed and the extraction attained balance in a short time. The method showed the obvious excellence of high recovery and enrichment factor, simplicity, rapidness and low cost.

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Room-temperature ionic liquids (RTILs) are a kind of melting salt systems composed by organic cations and organic or inorganic anions. They emerge as possible "green" solvents [32,33] and have a wide utilization in synthesis [34], catalysis [35,36] separation [37] and electrochemistry [38] for their unique properties such as low volatility, chemical and thermal stability, and good solubility for both organic and inorganic molecules. In recent years, the RTILs have attracted increasing interest and are applied more and more as the extraction solvent replacing the volatile solvent in sample preparation [39]. However, most were conducted in the liquid–liquid extraction and large volume of ionic liquid was required [40,41], which is tedious and costly. Then the microextraction based on ILs was developed by Liu et al. [42]. The ionic liquids were used in liquid-phase microextraction (LPME) or SDME. The temperature controlled ionic liquid dispersive liquid-phase microextraction (TCIL-DLPME) was evaluated for determination of the organophosphorus pesticides in water samples [43] and the mercury in water samples [44]. In the TCIL-DLPME, the sample was heated in water to 80 °C after the addition of IL. The IL mixed with the solution entirely at this temperature and thereafter the solution was cooled with ice-water for a certain time. The IL and aqueous phases were separated after centrifugation. Extraction was accomplished during the temperature rise and fall process. There are some limitations of ionic liquids application incompatible with gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS) due to their nonvolatility, however, some coupling could be realized with special techniques. Eva Aguilera-Herrador and his coworkers made ionic liquid based single-drop microextraction direct couple to GC/MS by adopting a new and removable interface [46].

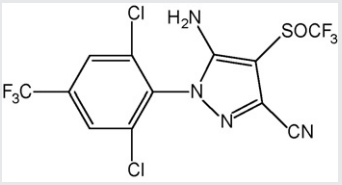
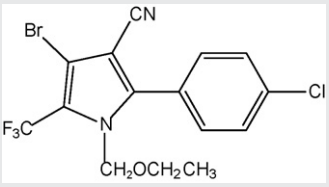
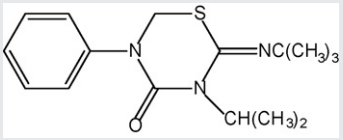
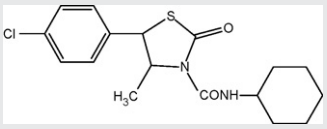
In this paper, we focus on investigating dispersive liquid–liquid microextraction based on ionic liquid. Use of IL can replace use of highly toxic, chlorinated solvents, usually employed as extractants in DLLME, and allows facile injection into reversed-phase system after dilution. In comparison with temperature controlled ionic liquid dispersive liquid-phase microextraction, this process avoids the heating and cooling step, which may lead to the degradation of some thermal unstable compound or other unexpected effects, and significantly reduces the extraction time. Besides, IL-DLLME has important advantages over conventional extraction techniques, since it is fast, easy to operate and avoids using highly toxic chlorinated solvents. We assess the IL-DLLME technique combined with HPLC for determination four insecticides at the ppb level in some real water samples. The effect of experiment parameters on the extraction efficiency including type, volume of IL, disperser solvent, pH, salt addition, extraction time and centrifuge time were investigated and optimized.

2. Experimental

2.1. Reagents and materials

The studied insecticides (fipronil, chlorfenapyr, buprofezin, and hexythiazox) (Table 1) prepared in methanol were obtained from Agricultural Environmental Protection Institution in Tianjin, China. 1-Hexyl-3-methylimidazolium hexafluorophosphate [C_6MIM][PF_6] was obtained from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. The dispersive solvent methanol, acetone, and acetonitrile (HPLC-grade) were purchased from Fisher Scientific (Fair Lawn, NJ, USA). Sodium chloride (analytical grade) and acetic acid were obtained from Beijing Chemical Reagent Company.

Table 1
Chemical structures and log K_{ow} of the insecticides.

Insecticide	Structure	log K_{ow}
Fipronil		4.0
Chlorfenapyr		4.83
Buprofezin		4.3
Hexythiazox		2.53

Stock solutions of 1000 mg/L for each insecticide were dissolved in methanol and were stored at −20 °C. Mixed standard solution of 20 mg/L of each pesticide was prepared in methanol. Chromatograms and peak areas were obtained for quality control and the calculation of enrichment factors and recoveries by injecting mixed standard solutions into the instrumental system five times a day. The working solutions were prepared by serial dilutions of the mixed standard solution with ultra pure water before extraction. The sodium chloride solution was prepared by dissolving 5.0 g NaCl into 50 mL pure water.

Tap water, lake water and fountain water used for the validation of the method were collected in glass bottles from main area of Beijing, Taihu, and Beijing, China, respectively. The water samples were analyzed in advance and were found free of selected insecticides. No previous treatment was conducted in tap water; lake

Table 2
Quantitative results.

Insecticide	Linearity	Correlation coefficient (R^2)	LODs (μg/L)[a]	RSD (%)[b]	Enrichment factor[c]	Recovery (%)
Fipronil	$y = 2.201x - 2.467$	0.9967	0.53	4.5	238	84
Chlorfenapyr	$y = 1.617x - 2.733$	0.9950	1.05	10.5	209	79
Buprofezin	$y = 1.52x - 3.6$	0.9973	1.12	6.8	254	96
Hexythiazox	$y = 1.598x - 9.2$	0.9947	1.28	9.3	276	106

[a] LOD values are calculated from aqueous sample spiked with 2.0 μg/L of each insecticide, S/N = 3;
[b] RSD values are calculated by average of five determination ($n = 5$) of each insecticide at spiked level of 5.0 μg/L.
[c] The enrichment factor is the ratio of the analyte concentration in the sediment and the initial analyte concentration in the aqueous sample, not considering the dilution with methanol (0.050 mL) before its final injection in the LC column.

water and fountain were filtered through a 0.45 μm membrane before analysis. All the water samples were stored in darkness at 4 °C.

2.2. Instrumentation

Chromatographic analysis was carried out on Agilent 1100 HPLC system equipped with a diode array detection (DAD) system and an automatic sample injector, The separation was performed on Agilent C18 column using methanol–water (78:22 v/v) as mobile phase. The flow rate was 1 mL/min and column temperate was 25 °C. The DAD wavelength was 215 nm. A RJ-TD-40B (Ruijiang, China) centrifuge was used for centrifugation. The pH measurements were performed with a model pHS-3C pH meter (Shanghai, China).

2.3. Extraction procedure

A volume of 5.0 mL of spiked water at 20 μg/L level for each insecticide was placed in a 10-mL glass test tube with conical bottom. A mixture of 0.052 g [C_6MIM][PF_6] (extraction solvent, because it is too viscous to be exactly transferred by syringe, we quantified it by weighting with electronic balance) and 0.50 mL methanol (disperser solvent) was quickly injected into a sample solution with a 1 mL syringe (Shanghai, China). Cloudy solution was quickly formed as the fine droplet dispersed the immiscible extraction solvent in the aqueous sample which greatly enlarged the contact area between the extraction solvent and aqueous phase. The analytes in aqueous sample were extracted into the fine ionic liquid droplets at this step. Then the water–methanol–[C_6MIM][PF_6] mixture was centrifuged at 4000 rpm for 10.0 min. After this process, the dispersive particles of ionic liquid phase were sedimented in the bottom of conical test tube. The upper aqueous phase was removed with a syringe, and the IL phase (about 19 μL) was dissolved in 50 μL methanol and 10 μL was injected into the HPLC system for analysis. The extraction steps are illustrated in Fig. 1.

3. Results and discussion

3.1. Optimization of IL-DLLME

To obtain the high enrichment factors and recoveries, the parameters which affect the partition of analytes among the different phases were optimized using mixed working solutions. A step-by-step optimization scheme was designed for analysis including the type and volume of extraction and disperser solvent, the extraction time, pH of the aqueous samples, salt addition and effect of disperser solvent. In order to calculate the enrichment factor and recovery, Eqs. (1) and (2) were used.

$$\mathrm{EF} = \frac{C_{\mathrm{sed}}}{C_0} \tag{1}$$

where EF, C_{sed} and C_0 are the enrichment factor, the analyte concentration in the sediment and the initial analyte concentration in the aqueous samples, respectively.

C_{sed} was calculated from the calibration graph of insecticide standard solution in the concentration range of 0.2–5.0 mg/L.

$$R\% = \frac{C_{\mathrm{sed}} V_{\mathrm{sed}}}{C_0 V_{\mathrm{aq}}} \times 100 = \mathrm{EF} \times \frac{V_{\mathrm{sed}}}{V_{\mathrm{aq}}} \times 100 \tag{2}$$

where $R\%$, V_{sed}, V_{aq}, are the extraction recovery, the volume of the sediment phase and the volume of the aqueous sample respectively.

3.1.1. Selection of ionic liquid

The development of such schemes requires a selection of suitable pure ionic liquids based on their properties among a large number of ionic liquids, the appropriate ILs for extraction in water samples should meet some requirements such as low solubility in water, good extraction ability for the target analytes, high density than water. And it should exist in the form of liquid in experiment. For these reasons, we focus on the inexpensive imidazolium-ILs [45] containing $[PF_6]^{6-}$ and side hydrophobic alkyl chain. They are of good solubility for organic molecule. In this experiment, 1-hexyl-3-methylimidazolium hexafluorophosphate ([C_6MIM][PF_6]) was selected.

3.1.2. Selection of disperser solvent

The key point for the selection of disperser solvent is the miscibility in both the IL phase (extraction solvent) and the aqueous sample. For this purpose, acetone, acetonitrile and methanol were selected in this procedure. A series of sample solutions were studied using 0.5 mL of each disperser solvent containing 0.052 g [C_6MIM][PF_6] (volume 40 μL, calculate from its density 1.30 g/mL), when using acetonitrile as disperser solvent, the mixture presented uniform transparent, and no sedimented phase was at the bottom of the conical tube after centrifugation. The acetonitrile, and IL formed

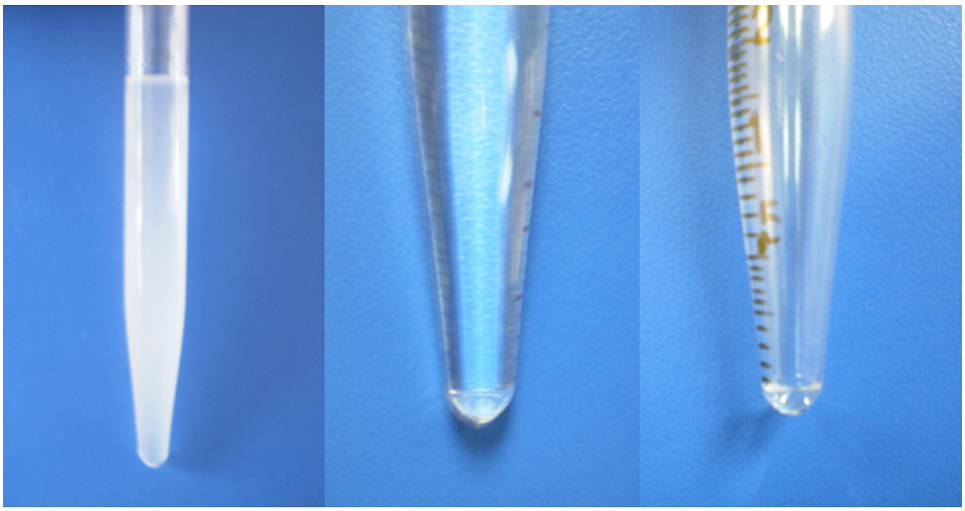


Fig. 1. Photography of extraction steps in IL-DLLME. (a) After adding 0.052 g IL and 0.5 mL methanol mixture in the sample solution and gently shaking; (b) after phase separation by centrifugation; (c) after removing the bulk aqueous phase.

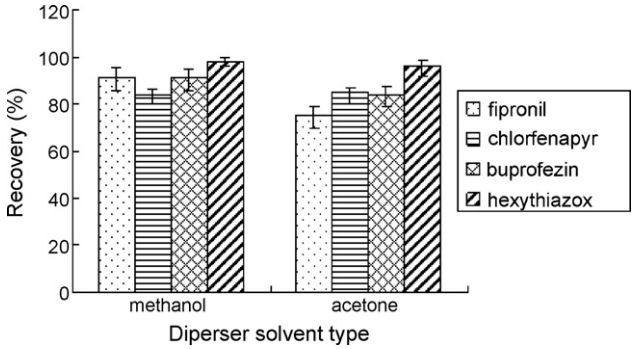


Fig. 2. Effect of disperser solvent on extraction efficiency. Extraction conditions: water sample volume, 5.00 mL; disperser solvent (methanol, acetone) volume, 0.50 mL; extraction solvent ($[C_6MIM][PF_6]$) 0.052 g. Spike level 20 μg/L.

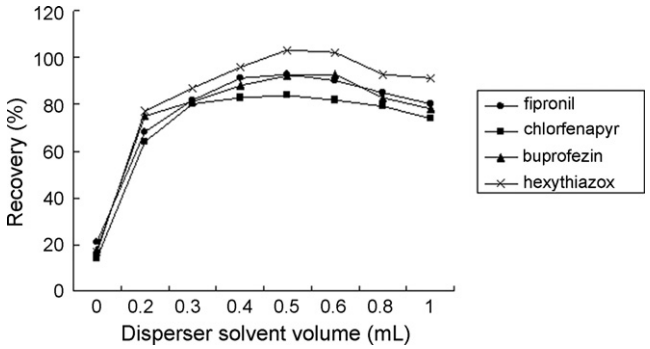


Fig. 4. Effect of volume of methanol on extraction efficiency. Extraction conditions: water sample 5.00 mL; extraction solvent $[C_6MIM][PF_6]$ 0.052 g, disperser solvent: methanol. Spike level 20 μg/L.

a miscible system. Therefore, acetonitrile was not a suitable solvent for helping extract the analytes. We would pay more attention to the other two solvents. The result was shown in Fig. 2. Recoveries obtained for each insecticide are between 74% and 98% with the two different disperser solvents. It was found the recovery of fipronil is higher by using methanol than when by using acetone, while similar recoveries were obtained for the other three insecticides. Therefore, methanol was selected as the disperser solvent for the subsequent experiments.

3.1.3. Amount of the ionic liquid

To evaluate the effect of this parameter, methanol with a constant volume containing different quantities of $[C_6MIM][PF_6]$ were tested in the same IL-DLLME procedure. The experiments were performed using 0.5 mL methanol, mixed with different amounts of $[C_6MIM][PF_6]$ (i.e., 0.030, 0.040, 0.052, 0.060, 0.080, 0.100 g) in 5 mL water sample at the spiked level of 20 μg/L. The sediment phase volume increased from 0 to 36.0 μL as the volume of the ionic liquid increased. With regard to Fig. 3, by increasing the amount of $[C_6MIM][PF_6]$ to 0.052 g, extraction recoveries for the four insecticides reached a constant level (81–103%) from 0.052 to 0 0.100 g. However, the enrichment factors decreased from 208–269 to 85–99 in the 0.052–0.100 g range as the volume of the sediment phase increased. Consequently, 0.052 g (40 μL) was used as the optimum quantity for the extraction in the further studies since the highest EFs were obtained at this quantity and the recoveries were acceptable.

3.1.4. Amount of the disperser solvent

In this study, the volumes of disperser solvent directly affect the IL solubility in water and the sedimented phase volume and thus influence the extraction efficiency and EF. To acquire its optimal volume, experiments were performed with different methanol volumes (0.20, 0.30, 0.40, 0.50, 0.60, 0.80 1.0 mL) containing 0.046, 0.048, 0.050, 0.052, 0.054, 0.056, 0.060, 0.064 g $[C_6MIM][PF_6]$, respectively. The quantity of $[C_6MIM][PF_6]$ changed simultaneously to remain the sedimented phase volume constantly (18.0 ± 1 μL) except that when the quantity of $[C_6MIM][PF_6]$ is 0.046 g, the sedimented phase is 15 μL. As shown in Fig. 4, the extraction efficiency increased by increasing the methanol volume to 0.5 mL. Further increase in the volume of methanol slightly reduced the enrichment factors. Therefore, the disperser solvent volume of 0.5 mL was chose as the optimum volume for further study.

3.1.5. pH

The effect of pH on IL-DLLME extraction efficiency was carried out in the pH range from 1 to 7 by adding 6 M HCl into the water samples. The result was shown in Fig. 5, For fipronil, chlorfenapyr, hexythiazox, no obvious variation in extraction recoveries can be seen when the pH was changed from 1 to 7, which means the acid addition may have little effect on the extraction efficiency for these compounds. While for buprofezin, the recovery decreased with pH decrease, at pH 1, the recovery decreased to 39%. The result could be interpreted that the molecule may present different formations at different pH environments, correlating with its acid-base property. Buprofezin, with a predicted pK_b value of 2.75, could be the ionic form at the low pH. So the buprofezgreadin extracted into the $[C_6MIM][PF_6]$ greatly decreased. Hence the use of acid and buffer was not required for the extraction in the subsequent experiments.

3.1.6. Salting out effect

In the conventional LLE, salt addition may improve the analyte's partition to the organic phase or diminish the solubility of

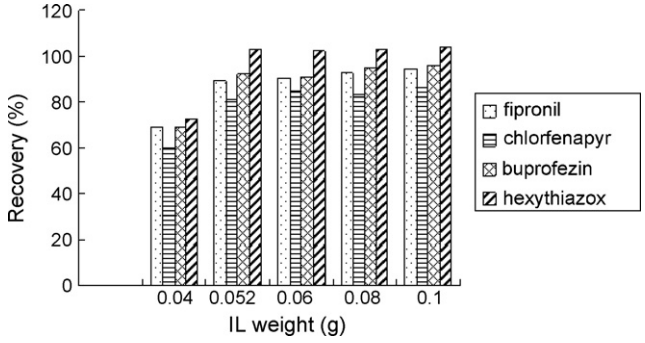


Fig. 3. Effect of the amount of $[C_6MIM][PF_6]$ on extraction efficiency. Extraction conditions: water sample volume, 5.00 mL; extraction solvent $[C_6MIM][PF_6]$. Disperser solvent 0.50 mL methanol. Spike level 20 μg/L.

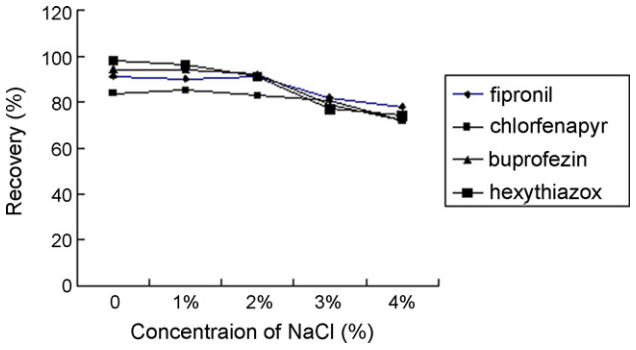


Fig. 5. Effect of addition of NaCl on the recoveries. Extraction conditions: water sample volume, 5.00 mL; extraction solvent $[C_6MIM][PF_6]$. 0.052 g, disperser solvent: 0.5 mL methanol. Spike level 20 μg/L.

the organic solvent in water phase. However, it may have different effects when ionic liquids are used as the extraction solvent. In order to investigate the salting out effect on the performance of IL-DLLME, series of experiments were performed by adding various amount of NaCl (0–5%, w/v) into fortified water samples with other conditions fixed. As shown in Fig. 5, with the NaCl concentration increasing, the volume of the sediment phase decreased from 19.0 to 12.0 μL and the recoveries decreased correspondingly. The enrichment factor increased as NaCl concentration increased. The result could be explained that the salt addition enhance the solubility of ionic liquid in water Then, salt addition was not used in further experiments.

3.1.7. Extraction time

Extraction involves a transferring process of target compounds from the aqueous phase into the ionic liquid phase which is time dependent. Maximum quantity of the target analytes is extracted into the ionic liquid phase when extraction equilibrium is obtained. The extraction time in this experiment was defined as the interval between injection of the mixture of methanol and ionic liquid and the moment centrifugation starts. To evaluate the optimum extraction time, experiments were carried out at a series of time intervals. The result can be seen in Fig. 6. The recoveries–time curve revealed that the extraction balance could be attained within 2 min, longer extraction time would not affect the extraction efficiency much. We could draw a conclusion that the extraction was a very fast process in the IL-DLLME, since after the formation of cloudy solution, the surface area between the IL droplet and the aqueous phase was very large, which was a key factor facilitating the equilibrium. Consequently, short time was required for extraction. Generally, the cloudy solution was laid for 3–4 min before centrifuging in this method.

3.1.8. Centrifugation time

Centrifugation plays an important role in separation procedure. The ionic liquid assembled in the conic tube bottom during this process. In order to investigate the centrifugation time, experiments were performed by centrifuging for 3, 5, 8, 10, 12, and 16 min respectively at 4000 rpm after extraction. The sedimented phase volume was 11.0 μL when centrifuging for 3 min, and increased to 19.0 μL when centrifuging for 10 min, then the sedimented phase had not obviously increased after longer centrifuging. As indicated in Fig. 7, the recoveries of all the analytes increased as the centrifugation time increased before 10 min. When it exceeded 10 min, the recoveries had no further increase. Therefore, 10 min was selected as the centrifugation time (Fig. 7).

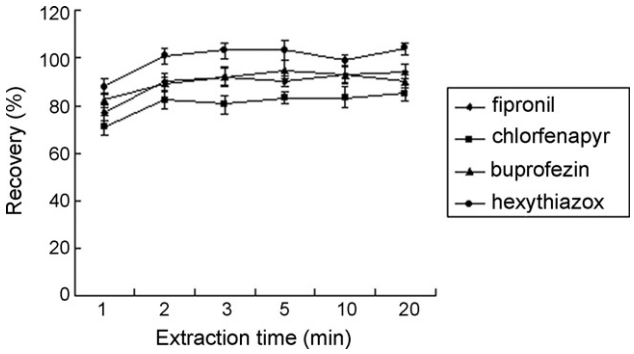


Fig. 6. Effect of extraction time on the recoveries. Extraction conditions: water sample volume, 5.00 mL; extraction solvent [C_6MIM][PF_6]. 0.052 g, disperser solvent: 0.5 mL methanol. Spike level 20 μg/L.

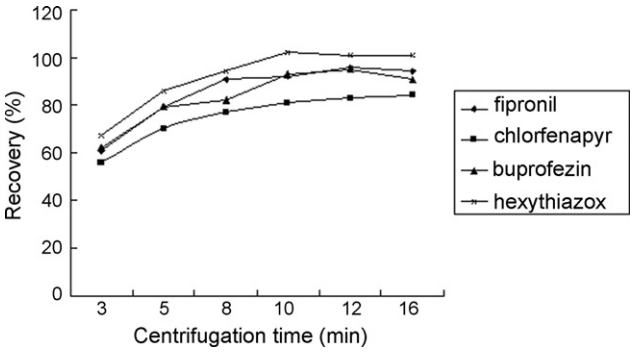


Fig. 7. Effect of centrifugation time on the recoveries. Extraction conditions: water sample volume, 5.00 mL; extraction solvent [C_6MIM][PF_6]. 0.052 g, disperser solvent: 0.5 mL methanol. Spike level 20 μg/L.

3.1.9. Influence of the disperser solvent on IL-DLLME

To investigate the influence of the dispersive solvent (in this study methanol) on IL-DLLME, experiments were carried out in different ways: (i) extraction was performed using 0.052 g [C6MIM][PF6] without methanol addition. Then it was vibrated for 10 min. (ii) Extraction was performed by injecting 0.052 g [C_6MIM][PF_6] into the sample which 0.5 mL methanol had been added previously and vibrating for 10 min. Finally (iii) extraction was performed by rapid injection of a mixture of 0.5 mL methanol containing 0.052 g [C_6MIM][PF_6] into the water sample. Results obtained were shown in Fig. 8. Method (iii) displayed the highest recoveries and EFs, (i) and (ii) showed lower extraction efficiency, while (ii) was comparatively higher than (i). The result indicated that dispersion of extraction solvent into water phase played pivotal role for efficiently extracting the analytes. It was noticeable that no cloudy solution formed in (i) and (ii), the large surface area between ionic liquid and the aqueous phase resulting from the fine droplet improved the extraction efficiency and thereby considerable EFs and acceptable recoveries were obtained.

3.2. Evaluation of method performance

Under the optimized condition, linearity, reproducibility, limits of detection and enrichment factors were investigated via analyzing series levels of spiked water samples to evaluate the proposed IL-DLLME method. Three replicate extractions were performed for each concentration level. Results were shown in Table 2. The calibration curve was linear in the range 2–100 μg/L for all the

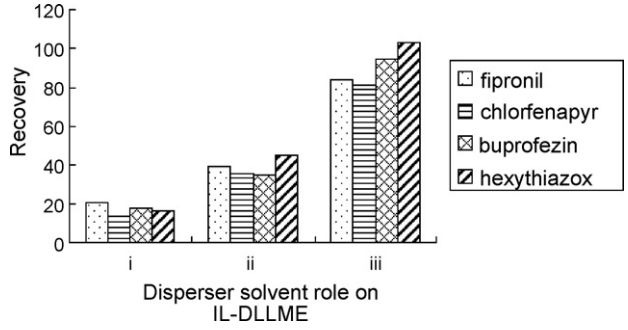


Fig. 8. Dispersive solvent role on IL-DLLME. Extraction conditions: water sample volume, 5.00 mL. (i) Extraction was performed using 0.052 g [C_6MIM][PF6] without methanol addition, then vibrating for 10 min. (ii) Extraction was performed by injecting 0.052 g [C_6MIM][PF_6] into the sample which 0.5 mL methanol had been added previously and vibrating for 10 min. Finally (iii) extraction was performed by rapid injection a mixture of 0.5 mL methanol containing 0.052 g [C_6MIM][PF_6] into the water sample. Spike level 20 μg/L.

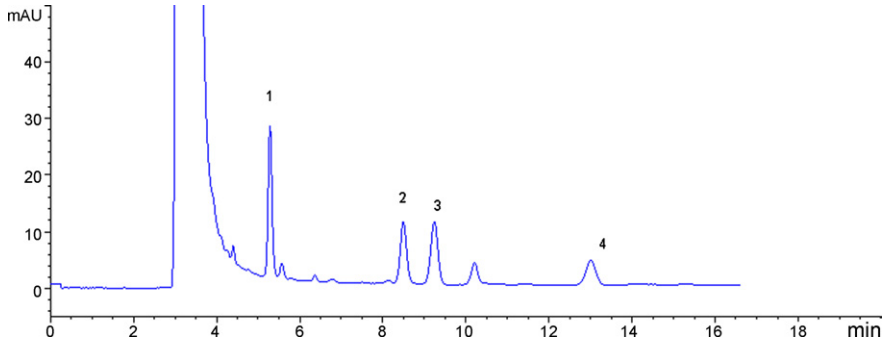


Fig. 9. Chromatogram for a lake water sample spiked at 20 μg/L. (1) Fipronil; (2) chlorfenapyr; (3) buprofezin; (4) hexythiazox.

Table 3
Recoveries of three real water samples with a spiked concentration of 5 μg/L and 20 μg/L for four insecticides.

Insecticide	Spiked level (μg/L)	Tap water		Lake water		Fountain water	
		Recovery (%)	RSD (%)*	Recovery (%)	RSD (%)*	Recovery (%)	RSD (%)*
Fipronil	5	92	5.2	89	5.7	84	5.2
	20	85	3.5	86	4.6	82	5.4
Chlorfenapyr	5	87	8.4	88	10.7	84	9.3
	20	82	5.4	84	5.3	79	8.5
Buprofezin	5	96	8.6	98	7.5	94	7.3
	20	95	6.1	94	4.5	91	6.5
Hexythiazox	5	106	9.5	110	8.4	104	9.2
	20	102	6.8	104	7.2	101	6.3

* RSD values are calculated by average of five determination ($n = 5$) of each insecticide.

Table 4
Comparison of IL-DLLME with other methods for the determination of insecticides in liquid samples.

Method	Sample volume (mL)	Analysis time (min)	Extraction solvent	LR μg L-1	Enrichment factor	References
SPE-GC/ECD	10	60	Hexane/dichloromethane	70–1000	10	[47]
SPME-GC/MS	3	45	–	0.3–100	30	[48]
LPME-GC/ECD	5	15	Isooctane	0.05–10	50	[49]
Represented method	5	5	Ionic liquid	2–100	200	Represented method

ECD, electron-capture detection.

insecticides, with the correlation coefficients from 0.9947 to 0.9973. The limit of detection (LOD) were calculated from purified water samples fortified level at 2 μg/L at a signal-to-noise (S/N) of 3 ranging from 0.53 to 1.28 μg/L. The precision of the method was investigated with spiked concentration of 5.0 μg/L for five replicates. And the RSDs of insecticides ranged from 4.5 to 10.5%, The extraction recoveries and enrichment factors of this method were high and ranged from 79 to 106% and 209 to 276, respectively.

3.3. Analysis of real water samples

In order to study the applicability of the proposed IL-DLLME method, experiments were performed with tap, lake and fountain waters spiked at concentration levels of 5 and 20 μg/L by adding insecticides standard solution into the water samples, respectively. For each sample, the extraction was repeated for five times. Recoveries obtained with precision were calculated and listed in Table 3. As can be seen, recoveries were between 79% and 110% and RSD values between 3.5% and 10.7% for all insecticides in the spiked samples. These results indicate that the matrices of the real water samples do not have obvious effect on the proposed IL-DLLME method for preconcentration of insecticides from water samples.

Typical chromatogram of four insecticides after DLLME in spiked water sample is shown in Fig. 9.

3.4. Comparison of IL-DLLME with other methods

The represented method is compared with the other methods for the extraction and determination the insecticides from liquid samples in Table 4. Some of the preconcentration methods of this table are solid-phase extraction, solid-phase microextraction, liquid-phase microextraction. As can be seen, the superiorities over the other methods are: (i) instead of the volatile organic solvent, ionic liquid is used as the extraction solvent, which is more safe and environment friendly; (i) small sample volume (5 mL) is adequate for analysis owing to the high enrichment factors (over 200); (iii) simple operation procedure make the sample preparation very easy and rapid, only a few minutes are needed before instrumental analysis. In conclusion, IL-DLLME presents a simple, fast, low sample consumption and environmental friendly technique that can be used for the preconcentration of some pesticides from liquid samples.

4. Conclusion

In this study, a new method IL-DLLME was developed combined with HPLC-DAD for determination of the four commonly used insecticides in water samples. The room-temperature liquid $[C_6MIM][PF_6]$ dispersed by methanol was firstly introduced into

microextraction for determination of these analytes in water samples. Enrichment factors were over 200 and the recoveries were acceptable for the pesticide residue analysis. The nonvolatile ionic liquid reduces the exposure danger in comparison with conventional organic solvent used for extraction and it improved the stability and limit of detection in single-drop mircroextraction because it is performed without the suspending procedure and the extraction volume is increased. IL-DLLME is proved to be a fast, simply, sensitive method and is expected to be widely applied for screening target compound in the future for sample extraction.

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